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Mercury emission from terrestrial background surfaces in the eastern USA. II: Air/surface exchange of mercury within forests from South Carolina to New England

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Abstract

Mercury air/surface exchange was measured over litter-covered soils with low Hg concentrations within various types of forests along the eastern seaboard of the USA. The fieldwork was conducted at six forested sites in state parks in South Carolina, North Carolina, New Jersey, Pennsylvania, New York and Maine from mid-May to early June 2005. The study showed that the Hg air/surface exchange was consistently very low and similar (overall daytime mean flux $= 0.2 \pm 0.9$ ng m^{-2} h^{-1}, $n = 310$, for all six sites monitored) with the various forest types. These flux values are comparable with those found in a year-long study in Tennessee (yearly daytime mean $= 0.4 \pm 0.5$ ng m^{-2} h^{-1}), but lower than many previous flux results reported for background soils. The Hg fluxes at all sites oscillated around zero, with many episodes of deposition (negative fluxes) occurring in both daytime and nighttime. While there were particular days showing significant correlations among the Hg air/surface exchange and certain environmental parameters, perhaps because of the low fluxes encountered, few significant correlations were found for any particular day of sampling between the Hg flux and environmental parameters such as solar radiation, soil temperature, air temperature (little variability seen), relative humidity, and ambient air Hg concentrations. Factors driving the Hg exchange as previously found for enriched soils may not hold for these background litter-covered forest soils. The results suggest that spatial variations of the Hg air/surface exchange were small among these different forest types for this particular time of year.

1. Introduction

Modeling is a valuable tool for understanding the global biogeochemical cycle of Hg. Successful calibration and validation of any model relies on field measurements, which provide characterization of

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the environmental system and in situ documentation of the variation of the parameters of concern. Modeling the biogeochemical cycle of Hg is challenging, in part because of insufficient field measurements and incomplete characterization of the behavior of Hg in various environmental systems. This is especially true regarding the Hg exchange between air and terrestrial background surfaces. Field measurements of the Hg air/surface exchange for background terrestrial systems were typically performed over short time periods (Schroeder et al., 1989; Xiao et al., 1991; Kim et al., 1995; Carpi and Lindberg, 1998; Zhang et al., 2001; Nacht and Gustin, 2004; Ericksen et al., 2006). There is a need to systematically characterize the Hg air/surface exchange over longer temporal scales covering various types of terrestrial systems on larger spatial scales.

This paper presents the results of one of the two research efforts focused on measuring the Hg air/surface exchange over litter-covered forest floors with low Hg content. A year-long field study was conducted to examine the Hg air/surface exchange over a forest floor in Tennessee, a site with 4 distinct seasons in the eastern USA (see Kuiken et al., 2008). The results from that study showed that the Hg air/surface exchange was very low throughout the entire year ($0.4\ \mathrm{ng\ m^{-2}\ h^{-1}}$, $\mathrm{SD} = 0.5$, $n = 301$) with a slight seasonality probably associated with canopy cover (higher fluxes under open canopy). The study reported here focused on a systematic field effort to investigate the Hg air/surface exchange within various types of forests across eastern USA during one season. This study of spatial variability combined with the longer-term TN study provides information to better understand Hg behavior associated with forest floors.

2. Site description and methods

2.1. Site description

Mercury air/surface exchange was measured at six sites with different forest types over a broad geographical region along the eastern seaboard of the USA. The sites were selected so that different forest types would be sampled at roughly the same time from mid-May to early June 2005. The six sites selected were Myrtle Beach State Park located in South Carolina (SC), River Park North in North Carolina (NC), Double Trouble State Park in New Jersey (NJ), Bald Eagle State Park in Pennsylvania (PA), Letchworth State Park in upstate New York (NY), and Ferry Beach State Park in Maine (ME) (Fig. 1). A detailed description of the location, forest type, soil type, soil and leaf litter Hg concentrations, and soil and leaf litter moisture contents for each site is provided in Table 1. The sites were selected to be representative of undisturbed forest floors not impacted by human activity.

2.2. Field measurement operation

Mercury air/surface exchange was measured at each site for a minimum of two days with ~8 h of data collected each day (Table 2). Whenever permitted, efforts were made to sample continuously for up to 48 h (Table 2). At each site the Hg air/surface exchange was measured using two DFC flux chambers systems (Kuiken et al., 2008). A fixed dynamic flux chamber (TTU) made of polycarbonate plastic (30 cm in diameter, 7.5 cm in height, 707 $\mathrm{cm^2}$, 5.0 L in volume) was used to measure the fluxes at the master location of the site. A separate dynamic flux chamber (UNR) made of polycarbonate plastic (19.5 cm in diameter, 3 cm in height, 299 $\mathrm{cm^2}$, 0.8 L) was used to measure the Hg air/surface exchange at locations surrounding the master location. The following equation was used to determine the Hg air/surface exchange:

$$F = (C_o - C_i)Q/A$$

where (Q) is the sampling flow rate (1.5 L $\mathrm{min^{-1}}$) controlled by a mass flow controller inside the Tekran Hg analyzer. A detailed description of the DFC method and related calculations can be found in the companion paper (Kuiken et al., 2008). The two Tekran Hg analyzers used in this study were calibrated in the laboratory using an outer standard Hg vapor source placed in a refrigerated water bath set at 17.9 °C and also calibrated during the field trip using an internal secondary Hg source equipped by the Tekran mercury analyzer. Consistent, satisfactory performance of the instruments was seen throughout the study. Along with emission fluxes, meteorological data including solar radiation, soil temperature, air temperature, wind speed/direction, relative humidity, and chamber temperature were also obtained (Table 2) using an HOBO weather station or manual meters in the same manner as described in the companion paper (Kuiken et al., 2008). In addition, soil and leaf samples were collected towards the end of the sampling period at each site to characterize the study sites. Leaf litter was collected by gloved hand until the topsoil was exposed. Leaf litter samples were

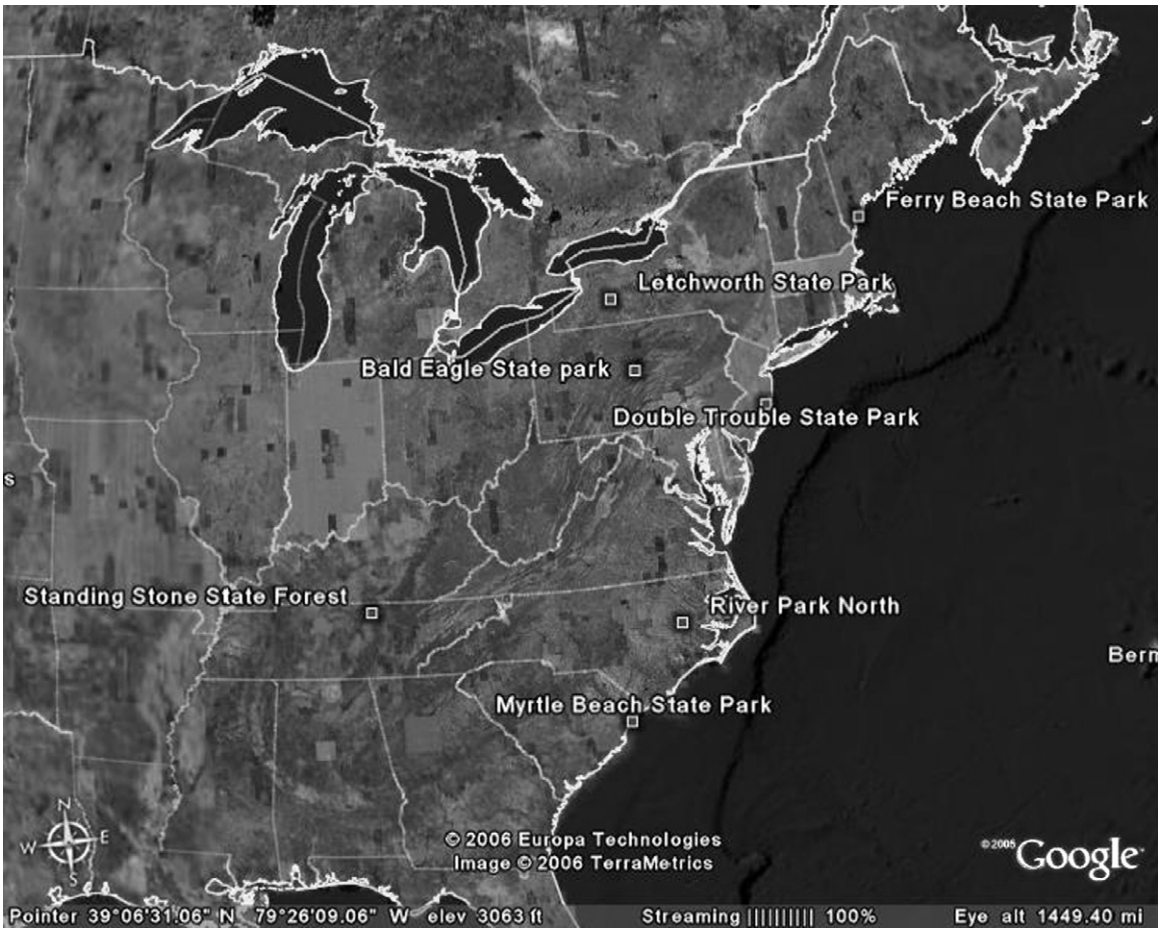

Fig. 1. The site map showing the locations and distributions of the six sampling sites of various forests from the south to the north across the eastern USA (Source: Google Earth).

sealed in clean plastic bags. Soil samples were taken with a soil auger (15 cm in sampling length) and sealed in clean plastic bags.

The chamber system blank was routinely inspected on site before and after the flux measurements were taken. The overall blank results were taken as the average of all chamber blank points for each particular day or from the entire period if continuous monitoring was conducted (Table 2). In most cases, the chamber blanks taken at the end of the sampling period were lower than the initial chamber blank. The chamber blank values were found to be very low (overall mean blank = 0.1 ± 0.1 ng m^{-2} h^{-1}) throughout the entire field study (Table 2). Because the mean blank values were not significantly different from zero, and following the precedence of earlier studies (Zhang et al., 2001), the flux and chamber blank values are provided here as originally obtained, and all the flux results are reported without correction for the chamber system blanks. A detailed discussion on the chamber system blank, its correction, and related issues are described in the companion paper (see Kuiken et al., 2008).

2.3. Comparison of field chambers

The UNR flux chamber was smaller with a shorter turnover time compared to the TTU flux chamber; on various occasions, leaf litter occupied a sizable part of the UNR chamber space. Fig. 2a and b compare the daytime Hg air/surface exchange measured at the six sites for the two different chamber systems. Fig. 2a shows similar mean fluxes obtained with the two chamber systems for each location; however, the data collected using the UNR chamber was slightly more variable. Fig. 2b combines the flux data for the two chambers during

Table 1
General site description and basic characteristics for all six sites sampled in the study

Location	State	Forest type[a]	Lat/long	Annual mean temperature (°C)	Monthly rainfall (mm)	Soil type[b]	Soil Hg concentration[c] (ppb)	Soil moisture[d] (%)	Leaf litter Hg concentration (ppb)	Leaf litter moisture (%)
Ferry Beach State Park (FBSP-ME)	ME	White-red-jack pine	43°28.6′N/ 70°23.5′W	9	95	Namburg sand	105 69	77 31	48	56
Letchworth State Park (LSP-NY)	NY	Maple-beech-birch	42°34.9′N/ 78°2.0′W	7	92	Varysburg gravelly loam	149 50	63 23	89	53
Bald Eagle State Park (BESP-PA)	PA	Oak pine	41°1.2′N/ 77°38.1′W	10	87	Andover very stony loam	219 33	61 19	65	63
Double Trouble State Park (DTSP-NJ)	NJ	Loblolly-shortleaf-pine	39°53.8′N/ 74°13.3′W	12	103	Lakehurst sand	122 13	68 23	47	60
River Park North (RPN-NC)	NC	Oak hickory	35°37.5′N/ 77°21.4′W	16	104	NA	66 21	58 10	34	48
Myrtle Beach State Park (MBSP-SC)	SC	Oak-gum-cypress	33°39.3′N/ 78°55.5′W	18	116	Lakeland sand	142 47	26 9	29	30

[a] The US Forest Service Classification System is followed.
[b] Soil type was determined using Natural Resources Conservation Service Web Soil Survey.
[c] Top soil is listed first followed by a ~15 cm soil sample taken with an auger.
[d] Soil moisture was determined from a ~15 cm soil sample taken with an auger.

Table 2
Summary of the mercury air/surface exchange fluxes for all sites monitored using the TTU chamber

State	Date	Start–stop (EST)	Duration (min)	Soil Hg flux (ng m^{-2} h^{-1})			SD	*n*	DFC blank (ng m^{-2} h^{-1})			Air Hg concentration (ng m^{-3})			SD	*n*
				Mean	Maximum	Minimum			Mean	SD	*n*	Mean	Maximum	Minimum		
Daytime[a]																
ME	5/27/05	1125–1725	360	0.6	1.5	0.2	0.3	19	0.0	0.1	2	1.8	2.4	1.4	0.3	19
ME	5/28/05	1025–1705	400	1.40	2.5	−0.1	0.6	21	0.2	0.2	2	2.0	2.4	1.4	0.3	21
ME	5/29/05	1055–1415	260	0.9	1.4	0.4	0.3	11	0.0	–	1	1.9	2.0	1.7	0.1	11
NY	5/31–6/2/05	7:00–19:00	1620	10.1	0.5	−0.5	0.2	81	–	–	–	1.4	1.6	1.1	0.1	81
NJ	5/18/05	1150–1750	360	−0.2	0.30	−0.3	0.1	19	0.1	0.1	3	1.9	2.2	1.7	0.1	19
NJ	5/19/05	1030–1650	380	−0.1	0.2	−0.2	0.1	20	0.1	0.0	3	1.8	2.1	1.6	0.1	20
NJ	5/21/05	1030–1730	420	0.0	0.7	−0.2	0.2	22	0.0	0.0	3	1.8	2.1	1.5	0.2	22
PA	6/4–5/05	7:00–19:00	740	0.3	1.8	−1.3	0.9	37	–	–	–	2.0	3.6	1.4	0.6	37
NC	5/14/05	1025–1725	420	0.7	1.3	0.1	0.3	22	0.5	0.3	2	2.5	3.2	2.1	0.3	22
NC	5/15/05	1045–1800	435	−0.3	1.5	−4.4	1.4	21	0.0	0.2	2	3.3	9.5	2.1	1.8	20
SC	5/11–12/2005	7:00–19:00	760	−0.2	1.9	−5.1	1.6	38	–	–	–	3.4	13.2	1.5	2.4	38
all	daytime	0700–1900	6200	0.2	2.5	−5.1	0.9	310	–	–	–	21.1	13.2	1.1	1.2	310
Nightime[b]																
NY	5/31–6/2/05	19:00–7:00	1440	−1.21	0.2	−0.3	0.1	72	_	_	_	1.2	1.3	1.1	0.0	72
PA	6/4–5/05	19:00–7:00	720	0.7	1.4	−0.6	0.5	36	–	–	–	1.6	2.5	1.2	0.4	36
SC	5/11–12/2005	19:00–7:00	680	−0.2	0.4	−0.7	0.2	34	–	–	–	1.7	2.3	1.3	0.3	34
Overall[c]																
NY	5/31–6/2/05	1325–1605	3060	−0.1	0.5	−0.5	0.1	153	0.0	0.0	4	1.3	1.6	1.1	0.1	153
PA	6/4–5/05	1305–1305	1440	0.5	1.8	−1.3	0.8	73	0.0	0.1	3	1.8	3.6	1.2	0.5	73
SC	5/11–12/2005	1745–1805	1445	−12	1.9	−5.1	1.31	72	0.2	–	1	2.6	13.2	1.3	1.9	72
Tennessee study[d]																
SSSF	5/21–22/04	1210–1150	1440	−0.2	0.6	−1.4	0.4	71	0.2	0.3	2	1.7	3.3	1.3	0.4	71
SSSF	5/21–22/04	7:00–19:00	720	−0.1	0.6	−1.2	0.4	36	–	–	–	1.7	3.3	1.3	0.4	36
SSSF	5/21–22/04	19:00–7:00	700	−0.3	0.1	−1.4	0.4	35	–	–	–	1.7	3.0	1.3	0.4	35
SSSF	8/16–17/04	1100–1100	1420	0.2	2.4	−0.9	0.6	73	0.4	–	1	1.4	2.2	0.9	0.2	73
SSSF	8/16–17/04	7:00–19:00	740	0.5	1.9	0.0	0.5	37	–	–	–	1.3	1.4	0.9	0.1	37
SSSF	8/16–17/04	19:00–7:00	720	−0.1	2.4	−0.9	0.5	36	_	_	_	1.5	2.2	1.0	0.2	36

[a] Represents the daytime data collected at each site from 0700 to 1900.
[b] Represents the nighttime data collected at each site from 1900 to 0700.
[c] Represents all the data collected at each site location.
[d] Standing Stone State Forest in Tennessee (Kuiken et al., 2008).

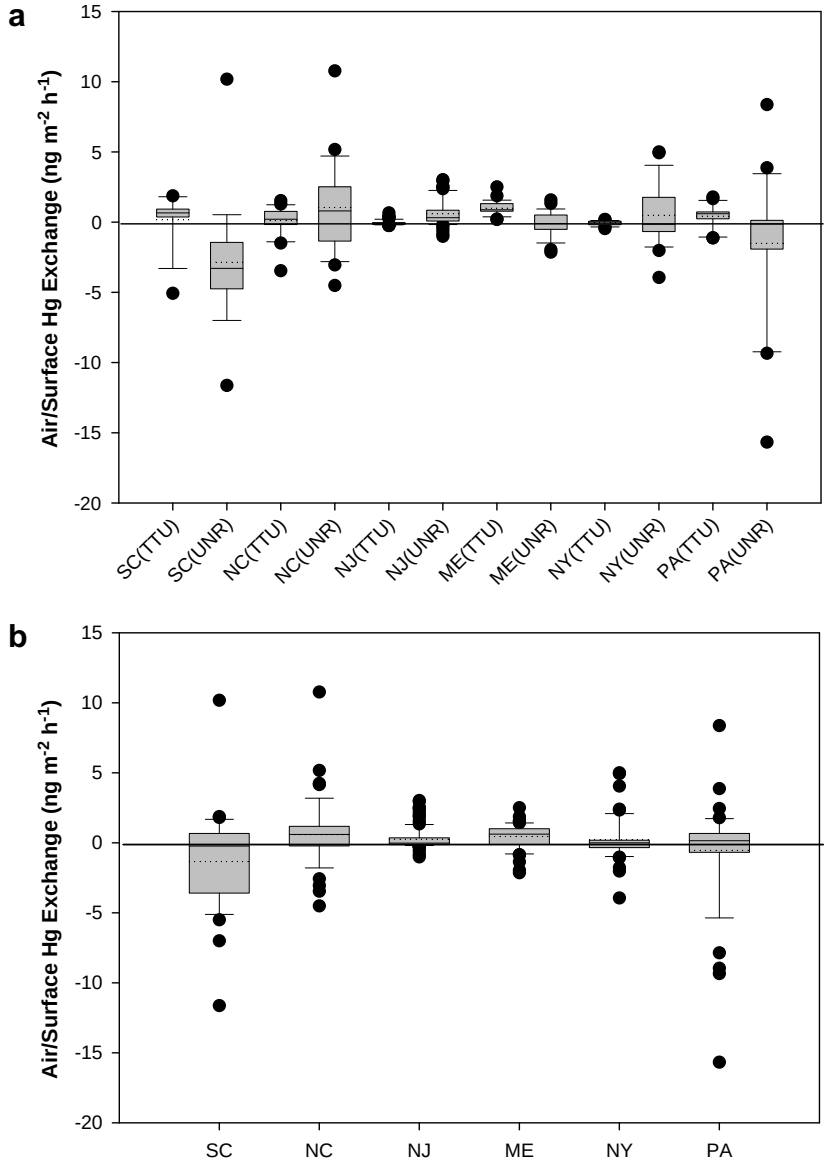

Fig. 2. Box and whisker plots comparing the daytime air/surface Hg exchange (a) the TTU chamber along with the UNR chamber, and (b) depicting the combined data from both the TTU and UNR chambers for each site sampled. The boundary of the box closest to zero indicates the 25th percentile, the boundary of the box farthest from zero indicates the 75th percentile, whiskers above and below the box indicate the 90th and 10th percentiles, the line within the box marks the median, the doted line represents the mean, and the dots above and below represent outliers.

the same sampling periods. Visual inspection of the data shows similar results for the two chambers. Statistical analysis using *t*-test suggests that the NC, NY, and PA sites showed little difference statistically, while the SC, NJ, and ME sites appeared to exhibit statistically different mean flux values. It should be noted, however, that the UNR chamber was moved throughout the day to obtain a spatial variation and representation of the Hg air/surface exchange, which could be responsible for the larger flux variations in association with the UNR chamber system.

3. Results and discussion

3.1. General magnitude and overall trend of mercury air/surface exchange within various forests

The field observations showed that the daytime Hg air/surface exchange was consistently very low

with 70% of the flux values $<0.5\ ng\ m^{-2}\ h^{-1}$. A large number of deposition fluxes were measured (~50%) and the daytime mean flux for all sites was $0.2\ ng\ m^{-2}\ h^{-1}$, SD = 0.9, $n = 310$ (Table 2). The general magnitude of the exchange fluxes varied slightly from state to state along with environmental conditions; however the mean fluxes were similar (Fig. 3). The mean daytime fluxes ranged from -0.3 to $1.0\ ng\ m^{-2}\ h^{-1}$, while the daytime maximum fluxes ranged from 0.0 to $2.5\ ng\ m^{-2}\ h^{-1}$ for all six sites (Table 2). On a geographical scale, while the air and soil temperatures varied from south to north (Table 3), the overall daytime Hg flux values did not vary significantly (Table 2). These findings indicate that despite variations in forest and soil type, these sites shared extremely low Hg air/surface exchange fluxes.

Linear regression analysis was conducted between environmental conditions and Hg air/surface exchange (Table 4). Similar to the results seen at Standing Stone State Forest (Kuiken et al., 2008), many of the air/surface exchange fluxes were at or below the detection limit of the system, which tended to obscure significant correlations with environmental parameters. The data analyses showed no significant correlation ($P < 0.05$) between solar radiation and the Hg air/surface exchange for the individual days (Table 4), except for the site in Maine. The forest canopy in Maine was not fully developed compared to the other sites (canopy at all other sites was 100% closed) and allowed more solar radiation to reach the forest floor. It is considered that when the forest canopy is fully developed, it removes the variability controlled by solar radiation that is present at sites void of a canopy, such as commonly seen for bare soils (Kim et al., 1995; Carpi and Lindberg, 1997; Gustin et al., 1997, 1999; Poissant and Casimir, 1998; Lindberg et al., 1999; Scholtz et al., 2003; Engle et al., 2006). Additional factors that could have influenced the air surface exchange at the Maine site were precipitation and soil moisture (both of which have been found to influence Hg emissions from soils). Just prior to sampling, a strong low-pressure system located off the coast of Maine for about a week produced heavy rains and unseasonably cool weather conditions. The sampling commenced on May 27, 2005, the day after the low-pressure system passed and the rain ended. Under these conditions the Hg exchange flux was found to correlate with solar radiation ($r = 0.80$, $P < 0.01$), air temperature ($r = 0.52$, $P < 0.01$), relative humidity ($r = 0.46$, $P < 0.01$), and air Hg concentration ($r = 0.47$, $P < 0.01$). Similar correlations were not found for the following two days of sampling (Table 4). Gustin et al. (2006) suggested that soil moisture and solar radiation worked synergistically to enhance Hg emissions. It is possible that this is

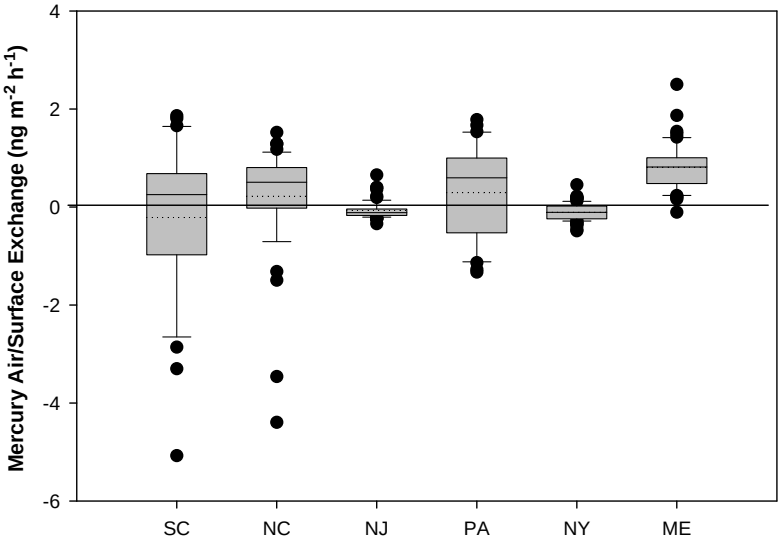

Fig. 3. A box and whisker plot summarizing the daytime Hg air/surface exchange fluxes for all six forested sites sampled using the TTU flux chamber (data collected between 0700–1900). The boundary of the box closest to zero indicates the 25th percentile, the boundary of the box farthest from zero indicates the 75th percentile, whiskers above and below the box indicate the 90th and 10th percentiles, the line within the box marks the median, and the doted line represents the mean, and the dots above and below represent outliers.

Table 3
Summary of the environmental conditions during the field monitoring of the forested sites and their statistical relationships with the air/surface exchange of mercury sampled using the TTU chamber

State	Date	Start–stop (EST)	Duration (min)	Solar radiation ($W m^{-2}$)					Soil temperature (°C)					Air temperature (°C)					Relative humidity (%)				
				Mean	Maximum	Minimum	SD	*n*	Mean	Maximum	Minimum	SD	*n*	Mean	Maximum	Minimum	SD	*n*	Mean	Maximum	Minimum	SD	*n*
Daytime																							
ME	5/27/05	1125–1725	360	139	614	26	139	19	11	11	10	0	19	14	16	13	1	19	80	85	74	3	19
ME	5/28/05	1025–1705	400	344	844	41	233	21	14	15	11	1	21	19	21	17	1	21	63	69	54	5	21
ME	5/29/05	1055–1415	260	376	717	144	216	11	13	14	12	1	11	16	17	15	1	11	70	75	63	4	11
NY	5/31–6/2/05	7:00–19:00	1620	99	392	17	62	81	12	14	11	1	81	20	26	9	4	81	54	97	35	19	81
NJ	5/18/05	1150–1750	360	86	191	31	37	19	13	13	13	0	19	17	18	16	0	19	39	45	33	3	19
NJ	5/19/05	1030–1650	380	96	351	38	67	20	13	13	12	0	20	17	18	16	1	20	46	56	40	5	20
NJ	5/21/05	1030–1730	420	108	416	17	95	22	13	13	11	1	22	18	19	16	1	22	51	62	46	4	22
PA	6/4–5/05	7:00–19:00	740	52	129	8	36	37	15	16	14	1	37	18	25	14	3	37	47	99	11	35	19
NC	5/14/04	1025–1725	420	100	239	43	43	22	17	18	16	1	22	25	26	21	2	22	70	81	62	7	22
NC	5/15/04	1045–1800	435	134	376	37	88	21	18	18	17	0	21	26	28	22	2	21	66	97	55	12	21
SC	5/11–12/2005	7:00–19:00	760	89	317	6	66	38	20	21	18	1	38	23	26	17	2	38	85	98	74	7	38
Nightime																							
NY	5/31–6/2/05	19:00–7:00	1440	5	41	1	9	72	12	13	11	1	72	15	24	9	4	72	79	97	41	17	72
PA	6/4–5/05	19:00–7:00	720	1	8	1	2	36	15	16	14	0	36	16	19	14	1	36	96	98	93	2	36
SC	5/11–12/2005	19:00–7:00	680	1	11	1	2	34	19	20	18	0	34	19	22	17	1	34	96	98	90	2	34
Overall																							
NY	5/31–6/2/05	1325–1605	3060	55	392	1	66	153	12	14	11	1	153	18	26	9	5	153	65	97	35	22	153
PA	6/4–5/05	1305–1305	1440	27	129	1	36	73	15	16	14	0	73	17	25	14	2	73	93	99	75	6	73
SC	5/11–12/2005	1745–1805	1445	48	317	1	65	72	19	21	18	1	72	21	26	17	3	72	90	98	74	8	72
SSSF	5/21–22/04	1210–1150	1420	28	109	1	34	71	21	22	20	1	71	24	28	21	2	71	72	84	60	7	71
SSSF	8/16–17/04	1100–1100	1460	26	97	1	31	73	18	19	18	1	73	20	24	16	3	73	73	92	52	10	73
Tennessee study																							
SSSF	5/21–22/04	7:00–19:00	720	53	109	4	31	36	21	22	20	1	36	26	28	21	2	36	68	84	60	7	36
SSSF	5/21–22/04	19:00–7:00	700	2	22	1	4	35	20	21	20	1	35	23	26	21	1	35	75	82	65	5	35
SSSF	8/16–17/04	7:00–19:00	740	50	97	4	27	37	19	19	18	1	37	21	24	16	2	37	69	92	52	12	37
SSSF	8/16–17/04	19:00–7:00	720	1	6	1	1	36	18	19	18	0	36	18	21	16	2	36	77	89	67	7	36

Table 4
Correlation with air/surface Hg exchange

State	Date/time	Flux vs. solar radiation		Flux vs. soil temperature		Flux vs. air temperature		Flux vs. relative humidity		Flux vs. air Hg concentration	
		r	*P*-value	*r*	*P*-value	*r*	*P*-value	*r*	*P*-value	*r*	*P*-value
All	Daytime	0.26	0.00	0.03	0.47	0.01	0.81	0.04	0.41	0.37	0.00
ME	5/27/05	0.89	0.00	0.16	0.52	0.72	0.00	0.68	0.00	0.69	0.00
ME	5/28/05	0.46	0.04	0.00	0.99	0.24	0.30	0.34	0.13	0.66	0.00
ME	5/29/05	0.28	0.40	0.10	0.77	0.24	0.48	0.20	0.55	0.08	0.82
NY	5/31–6/2	0.12	0.13	0.41	0.00	0.18	0.03	0.16	0.05	0.30	0.00
PA	6/4–6/5	0.11	0.34	0.48	0.00	0.32	0.01	0.31	0.01	0.56	0.00
NJ	5/18/05	0.12	0.62	0.50	0.03	0.65	0.00	0.27	0.25	0.17	0.49
NJ	5/19/05	0.17	0.48	0.11	0.64	0.30	0.20	0.20	0.40	0.34	0.14
NJ	5/21/05	0.22	0.34	0.54	0.01	0.58	0.00	0.47	0.03	0.29	0.19
NC	5/14/04	0.17	0.44	0.28	0.21	0.26	0.25	0.32	0.15	0.42	0.05
NC	5/15/04	0.29	0.21	0.32	0.16	0.74	0.00	0.88	0.00	0.78	0.00
SC	5/11–5/12	0.09	0.47	0.28	0.02	0.07	0.55	0.05	0.67	0.60	0.00
SSSF	5/21–5/22/04	0.11	0.34	0.18	0.13	0.14	0.25	0.06	0.60	0.60	0.00
SSSF	8/16–8/17/04	0.45	0.00	0.13	0.28	0.08	0.53	0.15	0.20	0.63	0.00
Day/night											
NY	7:00–19:00	0.18	0.12	0.52	0.00	0.37	0.00	0.32	0.00	0.46	0.00
NY	19:00–7:00	0.19	0.11	0.22	0.06	0.12	0.30	0.12	0.31	0.15	0.20
PA	7:00–19:00	0.11	0.52	0.69	0.00	0.65	0.00	0.58	0.00	0.58	0.00
PA	19:00–7:00	0.21	0.21	0.11	0.51	0.06	0.73	0.02	0.90	0.32	0.06
SC	7:00–19:00	0.13	0.42	0.34	0.04	0.12	0.47	0.09	0.59	0.67	0.00
SC	19:00–7:00	0.46	0.01	0.08	0.65	0.20	0.26	0.23	0.20	0.09	0.59
SSSF(5/21–5/22)	7:00–19:00	0.29	0.09	0.01	0.95	0.01	0.96	0.06	0.73	0.54	0.00
SSSF(5/21–5/22)	19:00–7:00	0.26	0.13	0.02	0.89	0.16	0.36	0.24	0.16	0.72	0.00
SSSF(8/16–8/17)	7:00–19:00	0.10	0.57	0.69	0.00	0.59	0.00	0.66	0.00	0.49	0.00
SSSF(8/16–8/17)	19:00–7:00	0.01	0.93	0.27	0.11	0.23	0.18	0.22	0.19	0.52	0.00

why more significant correlations were seen on the first day. It is interesting to note that the mean air/surface exchange flux for the 3 days sampled was 0.8 ± 0.5 ng m^{-2} h^{-1}, $n = 51$ (for values of individual days, see Table 2).

3.2. Comparison of mercury air/surface exchanges at various sites

Fig. 3 summarizes the Hg air/surface exchange rates at the six sites (TTU master location) sampled

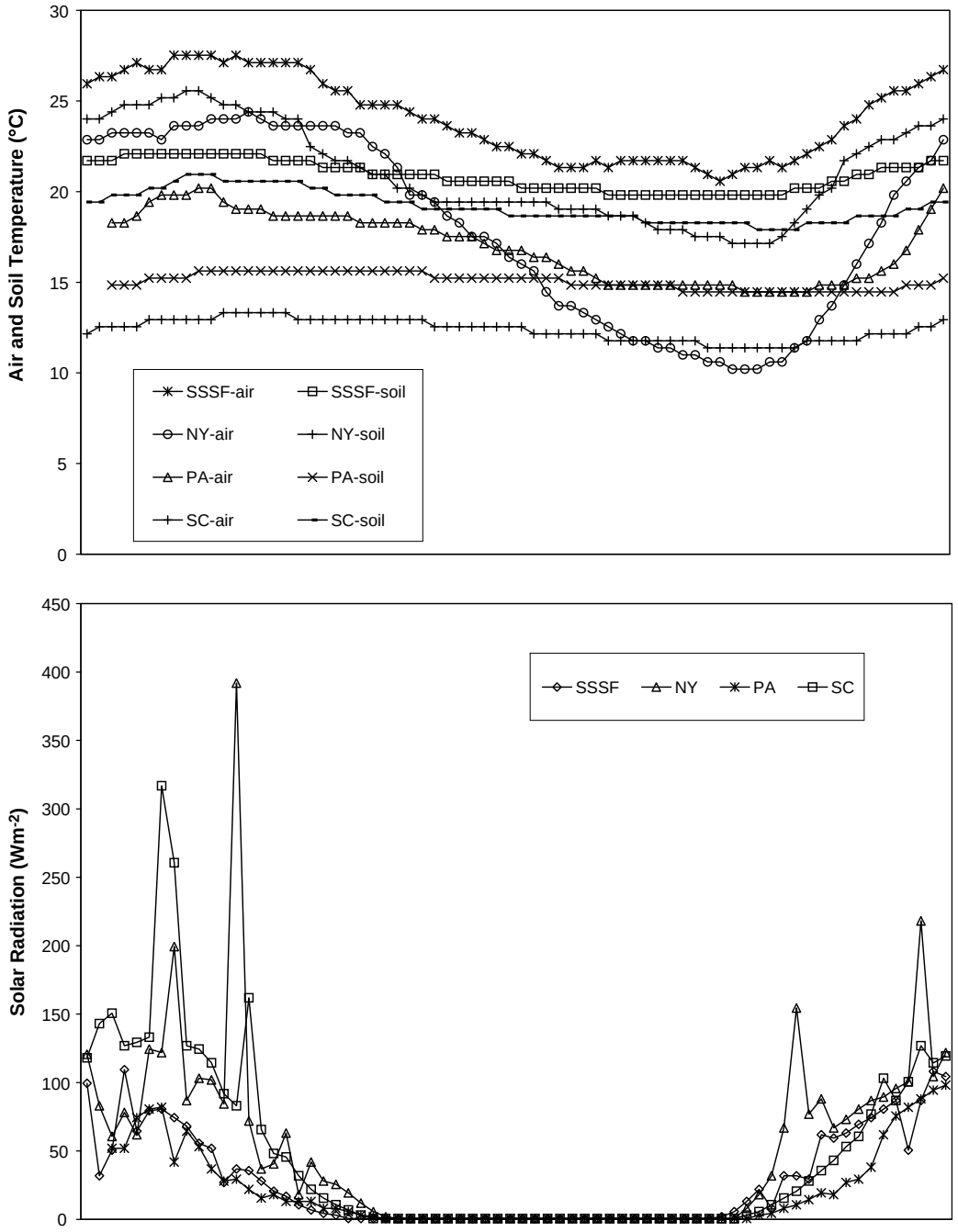

Fig. 4. 24-h Hg air/surface exchange for the sites in New York, Pennsylvania, South Carolina, and Tennessee (Standing Stone State Forest) along with solar radiation and air and soil temperature (all data shown, time 0 represents 12.30 pm).

(daytime fluxes only, 7 am–7 pm). All the sites exhibited fluxes that fluctuated around zero, although the data distribution from site to site differed. Fig. 3 also shows that the Hg air/surface exchange at these six sites was similar despite varying forest types, weather conditions, and geographical locations.

The NC, SC, and PA sites exhibited more variability in fluxes than the other sites. Slight variations in flux could be attributed to local weather conditions (Table 3). For example, while sampling in NC a thunderstorm passed through; in South Carolina, occasional spikes in solar radiation occurred in relation to gusts of wind and cloud cover, which allowed bursts of light to reach the forest floor; the PA site was relatively cloudy and humid during sampling and it had been raining the previous day. Another factor that may have increased flux variability is air Hg concentration. Mean air Hg concentrations were 2.6, 2.5, and 3.3 ng m^{-3} for the SC, NC, and PA sites, respectively. These are higher than the means for the other sites (all $\leqslant$ 2 ng m^{-3}), while the maximum air Hg concentrations for the three sites were 13.2, 3.2, and 9.5 ng m^{-3}, respectively, and were much higher than for other sites. A close inspection of the flux data for the SC and NC sites indicated that the episodes of negative fluxes occurred corresponding to the occurrence of high levels of the ambient air Hg concentrations at the sites. Lindberg et al. (2002) reported a similar phenomenon for Hg fluxes over a wetland. While individual points during these episodes appear to correlate, overall, the entire sampling period does not.

3.3. 24-h continuous flux sampling studies

To examine the overall influence of solar radiation on the air/surface exchange of Hg as well as the general exchange trends, at four separate sites (TN, NY, PA, and SC) Hg fluxes were measured continuously for at least 24 h. Fig. 4 depicts the Hg air/surface exchange at the four sites compared with soil and air temperature and solar radiation starting at 12.30 pm and running for 24 hours. Table 2 provides detailed results from the sites sampled with the TTU chamber only.

Although there was not statistical difference between night and daytime fluxes, the latter were more variable. The PA site showed higher mean flux value during the evening. There was no clear diel pattern associated with solar radiation or soil and air temperature, which followed typical diel patterns. The NY site exhibited constant diel flux.

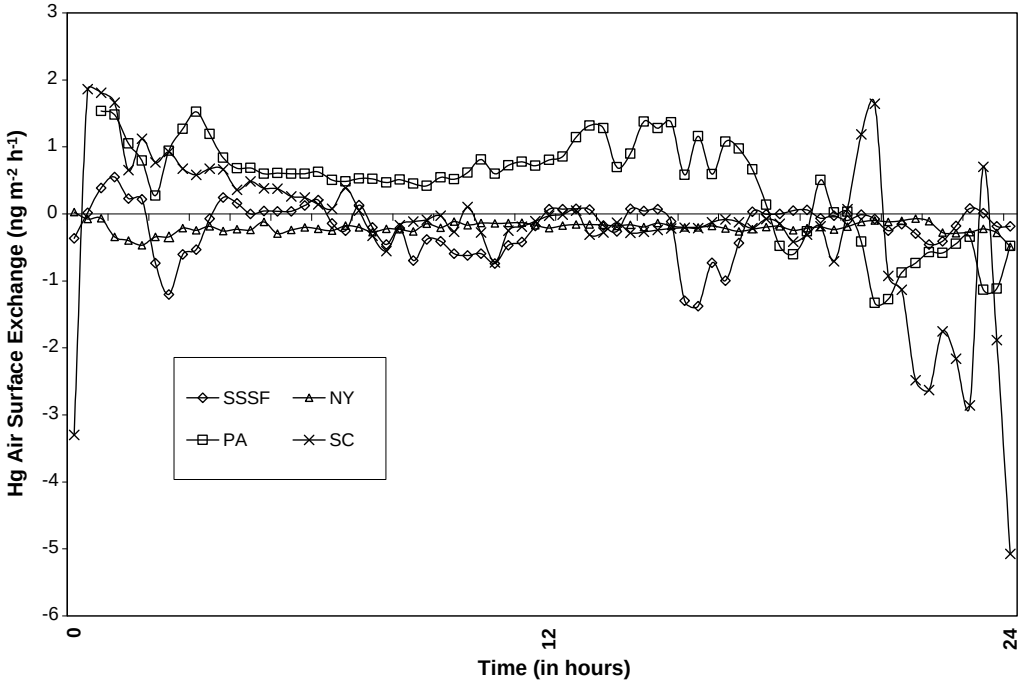

Fig. 4 (*continued*)

The overall stability at this site could be associated with stable weather conditions seen throughout the sampling period (Table 3). Two separate 24 h periods (May 21 and August 16, 2004) were sampled at the TN site (for details of forest type, see Kuiken et al., 2008). The Hg air/surface exchange for May at the TN site was generally higher than for August, while the overall variations were small (Fig. 4 and Table 2).

3.4. Comparison of this study with that at Standing Stone State Forest in Tennessee

The mean daytime Hg air/surface exchange for the six forest sites along the eastern seaboard of the USA during May–June 2005 was 0.2 ± 0.9 ng m^{-2} h^{-1}, compared to 0.4 ± 0.5 ng m^{-2} h^{-1} from Standing Stone State Forest in Tennessee during the year 2004. Hg air/surface exchange measured for the spring at the Tennessee site (0.0 ± 0.3 ng m^{-2} h^{-1}) was comparable for that measured for the six forested sites.

The data suggests that Hg air/surface exchange from forest floors in the eastern USA is different from enriched soils with respect to the Hg air/surface exchange and should clearly be treated differently when scaling or modeling. Litter-covered soils may not exhibit similar behavior to bare soils. Gustin et al. (2004) suggested that the presence of vegetation that shields soil surfaces from incident light reduces Hg emissions from enriched soils. This phenomenon may explain the results seen within the forested systems studied here. The general magnitude of the Hg air/surface exchange found from the eastern forest sites was very low to extremely low (generally < 1.0 ng m^{-2} h^{-1}). The lack of any significant correlations between the exchange fluxes and meteorological parameters seems to suggest that the factors driving the Hg exchange previously reported for different systems and bare soils (Carpi and Lindberg, 1997; Gustin et al., 1997, 1999; Kim et al., 1995; Poissant and Casimir, 1998; Scholtz et al., 2003) may not hold for litter-covered surfaces associated with background systems.

4. Conclusions

This study carried out within various types of forest systems across a vast region from the south (South Carolina) to the north (Maine) in the eastern USA during the same season (mid-May to early June) indicated Hg air/surface exchange rates that were consistently very low (overall daytime mean flux $= 0.2 \pm 0.9$ ng m^{-2} h^{-1}, $n = 310$, for all six sites monitored), irrespective of the forest type, soil type, and variations in weather conditions. These flux values are comparable with those seen in a year-long study conducted within Standing Stone State Forest in Tennessee (yearly daytime mean $= 0.4 \pm 0.5$ ng m^{-2} h^{-1}) but lower than many previous flux results obtained for non-litter-covered background soils. The Hg air/surface exchange fluxes at all the sites exhibited comparable trends fluctuating around 0 ng m^{-2} h^{-1}, with many episodes of deposition (negative fluxes) occurring in both the daytime and nighttime (~50% of the 30 min fluxes). While there were particular days showing significant correlations among the Hg air/surface exchange and certain environmental parameters, there were no consistent correlations found across the complete data set. Measured Hg air/surface exchange was lower than values published for bare soils at background/nonenriched sites. Data showed relatively the same flux values across a broad area for one time of year indicating that in scaling fluxes from forest floors at least along the eastern seaboard a common value may be applied. However, based on the seasonal data collected at the TN site temporal variability is important to consider. Thus in scaling Hg fluxes for eastern forested background systems, the flux from litter covered forest floors could be modeled collectively on a seasonal time step.

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